STANFORD UNIVERSITY LIBRARIES
1933
LIBRARY

UNIVERSITY OF VIRGINIA
SCHOOL OF CHEMISTRY

THE FREE ENERGIES OF FORMATION OF VARIOUS FORMS OF LEAD MONOXIDE

BY

JOHN HULON MOTE

This article is a reprint of a paper based upon a dissertation submitted to the Graduate Faculty of the University of Virginia in candidacy for the degree of Doctor of Philosophy

JUNE, 1929

3781
V81M
UNCLASSED
Dissertation

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

UNIVERSITY OF VIRGINIA
SCHOOL OF CHEMISTRY

THE FREE ENERGIES OF FORMATION OF VARIOUS FORMS OF LEAD MONOXIDE

BY

JOHN HULON MOTE

This article is a reprint of a paper based upon a dissertation submitted to the Graduate Faculty of the University of Virginia in candidacy for the degree of Doctor of Philosophy

JUNE, 1929

Easton, Pa.
Mack Printing Company
1932

ACKNOWLEDGMENT

I take this opportunity to express my appreciation and gratitude for the assistance received in this research from Dr. Hugh M. Spencer, at whose suggestion and under whose direction this work was carried out.

THE FREE ENERGIES OF FORMATION OF VARIOUS FORMS OF LEAD MONOXIDE

By John H. Mote[1]

Introduction

The free energies of formation of the various forms of lead monoxide are necessary links in the calculations of those of many other lead compounds. Smith and Woods[2] measured the potential of the cell

$$H_2(g),\ \text{dil. } Ba(OH)_2,\ PbO(\text{red}),\ Pb \qquad (1)$$

and thus with the $\Delta F^\circ_{298.1}$ of formation of water, $-56{,}560$ cal., found for that of the red lead monoxide, $-45{,}050$ cal.

Randall and Spencer[3] measured the solubility of the various forms of lead monoxide in dilute aqueous potassium hydroxide solutions and thus the free energies of formation of plumbite ion from the various forms. From the differences in free energies of formation of plumbite ion and Smith and Woods' evaluation of the ΔF of formation of the red form, one may derive that of the others.

In addition to determining the solubilities Glasstone[4] measured the electromotive forces of cells of the type

$$Pb,\ PbO,\ NaOH(1N),\ HgO,\ Hg \qquad (2)$$

using the eight different preparations of lead monoxide which he had used in the solubility measurements. The solubility measurements were interpreted as proving the identity except as to size of particles of the various preparations. The measurements were made at room temperatures, which were presumably around 20°, and the values for the cells are given to only three figures. He made no attempt to avoid diffusion potentials by placing lead monoxide in the mercuric oxide side of the cell. Glasstone assumed that the measurements of all the cells checked one another, in conformity with his solubility measurements, and gave 0.673 v. as the mean potential. In order to get the temperature coefficient he attempted some cells at 0 and 25° which he measured to one-tenth of a millivolt. For this purpose red and yellowish-green oxides were used. Only the electrode potentials are given, the value for the mercuric oxide

[1] Du Pont Fellow in Chemistry 1928–29.

[2] D. F. Smith and H. K. Woods, *J. Am. Chem. Soc.*, **45**, 2632 (1923).

[3] M. Randall and H. M. Spencer, *ibid.*, **50**, 1572 (1928). The results of the earlier solubility measurements are briefly discussed in this paper. Two papers including similar measurements have since appeared, by H. Töpelmann, *J. prakt. Chem.*, **121**, 320 (1929), and M. P. Applebey and H. M. Powell, *J. Chem. Soc.*, 2831 (1931).

[4] S. Glasstone, *J. Chem. Soc.*, **119**, 1914 (1921).

electrode by which he calculated the electrode potential from the cell potential being omitted. It seems likely that he used the value −0.1135 v. of Donnan and Allmand. He obtained for the red oxide an electrode potential of 0.5621 at 25° and for the yellow at the same temperature 0.5598 v. By combination with −0.1135 for the mercuric oxide electrode, the electromotive forces of the cells are 0.6756 and 0.6733 v., respectively, when the cells contain the red and yellow oxides.

Applebey and Reid[5] repeated the work of Glasstone and found $E_{293.1}$ = 0.6808 and 0.6734 v. Fried[6] measured similar cells in order to test the Nernst heat theorem. He used a lead-plated electrode and a Kahlbaum preparation of lead monoxide. The potentials varied considerably over two millivolts and since his measurements of the hydrogen–mercuric oxide cell showed much more satisfactory reproducibility, the fault seems to lie in the lead–lead monoxide electrodes. One may attribute the lack of reproducibility to inequalities in the completeness of saturation of the alkaline solutions by the lead oxide. At any rate the results cannot lead to significant free energy values since the lead oxide used was not a pure form.

In spite of the discrepancies in the potentials cited it appeared that potential measurements, in which the same care should be taken in the preparation of materials and the establishment of equilibrium by preshaking as was observed by Randall and Spencer, promised more definitive values of the differences of the free energies of formation of the oxides than were available from the solubility measurements. Moreover, since the free energy of formation of mercuric oxide is known to a fairly high degree of accuracy, measurements of cells of the type

Pb(in het. amalg.) PbO(red, yellow or hydrate), dil. $Ba(OH)_2$, HgO(red) + PbO(red, yellow or hydrate), Hg(l) (3)

afford a method of calculation of the free energies of formation of the lead monoxides independent of the one derived by Smith and Woods for the red form except in that both are dependent on the free energy of formation of water. Accordingly measurements of such cells are here presented.

Experimental Procedure

All reagents used in this investigation were of C. P. quality, and in most cases were further purified before they were used.

Mercury.—The mercury used in the cells and that used in the preparation of the lead amalgams, after the usual washing with mercurous nitrate, was thrice distilled at low pressure and was preserved in closed containers. No film was present on the surface of the mercury used in the experiments.

Lead.—The lead used was a chemically pure commercial variety designated as "Test Lead" and was silver-free.

[5] M. P. Applebey and R. D. Reid, *J. Chem. Soc.*, **121**, 2129 (1922).

[6] F. Fried, *Z. physik. Chem.*, **123**, 406 (1926).

Lead Amalgam.—The two-phase lead amalgam was prepared by heating together the lead and purified mercury in such proportion as to give a five per cent. amalgam.

Barium Hydroxide.—The barium hydroxide solution used as electrolyte and in the preparation of the hydrated oxide was made from a recrystallized C. P. product. It was made up and preserved out of contact with carbon dioxide.

Mercuric Oxide.—The mercuric oxide used was the red form.[7] It was prepared by letting chemically pure nitric acid react with distilled mercury and heating the nitrate thus formed until it had entirely decomposed, leaving mercuric oxide. The oxide was washed numerous times with conductivity water to remove the last traces of mercuric nitrate. It was stored under conductivity water.

Sodium Hydroxide.—Carbonate-free sodium hydroxide was prepared by the action of water vapor on metallic sodium in an atmosphere of hydrogen under a bell jar. The metallic sodium was suspended in a nickel gauze cone and the hydroxide formed was caught in a nickel crucible and preserved out of contact with air until ready for use.

Lead Monoxides.—The red and yellow lead monoxides[8] were prepared by a modification of the method of Geuther and of Ruer described by Randall and Spencer.[3] In the preparation of the red form usually the yellow modification formed first but on further heating changed over into the red. It was possible to form the red modification with the sodium hydroxide used in the preparation of the yellow. Dilution of the solution immediately after the yellow had formed and rapid cooling prevented the further change to the red. The homogeneity of the samples was proved by microscopic examination.

Hydrated Lead Monoxide.—The white hydrated lead monoxide was prepared by the method of Pleissner.[9]

---

[7] The identity of the red and yellow forms of mercuric oxide has been established by means of x-ray analysis (powder method) [G. R. Levi, *Gazz. chim. ital.*, **54**, 709 (1924); W. Zachariasen, *Z. physik. Chem.*, **128**, 421 (1927)]. The two oxides give slightly different electromotive forces but the difference may be accounted for on the basis of difference in solubility due to difference in size of particles.

[8] The individuality and allotropy of these two forms of lead monoxide have been the subject of numerous papers in addition to the solubility measurements referred to above. V. Kohlschütter and P. Scherrer [*Helv. Chim. Acta*, **7**, 337 (1924)] proved them to be different by x-ray analysis and their ultimate structures have been determined by further use of the same methods. The results, except those of M. LeBlanc and E. Eberius [*Z. physik. Chem.*, **160A**, 69 (1932)], are summarized by J. A. Darbyshire [*J. Chem. Soc.*, 211 (1932)]. It appears certain that there are only two polymorphic forms of lead monoxide and the authors believe the variations in color are caused (1) by varying size of particles, (2) by varying amounts of the two forms and (3) by the presence of varying amounts of metallic lead.

[9] M. Pleissner, *Arb. kais. Gesundh.*, **26**, 384 (1907). The same method was used by Randall and Spencer,[3] whose analysis gave 89.8% Pb. H. Töpelmann[3] using two other methods of analysis, found for the Pleissner preparation 89.75 and 89.84% lead and 89.82 and 89.73% lead for a preparation following the directions of E. Müller, in which 2 *N* sodium hydroxide was used in place of the barium hydroxide in the Pleissner preparation. Randall and Spencer dried the hydrate in a vacuum desiccator over sulfuric acid (30–40%), whereas Töpelmann's products were dried with alcohol and ether and finally over calcium chloride in a vacuum desiccator. G. F. Hüttig and B. Steiner [*Z. anorg. allgem. Chem.*, **197**, 258 (1931)] prepared the hydrated oxide by two other methods and subjected the products to isobaric dehydration and x-ray analysis. Their hydrate No. 1 ($PbO \cdot 0.504H_2O$) was prepared by the addition at 0° of a lead acetate solution (185 g. in 1000 cc. of water) in a jet to 1000 cc. of 14 *N* ammonia. After shaking, the white crystalline precipitate was washed with water, filtered and dried over 30%

Preparation of the Cells.—The vessels used as cells were modifications of the usual H-type vessels. They consisted of two sets of three electrodes connected by a cross arm, thus nine combinations could be obtained with the six electrodes. The mercury, amalgams and mercuric oxide were first put into place. The barium hydroxide solution, saturated by shaking with the lead monoxide, along with excess of the monoxide was then added and nitrogen was bubbled alternately through the various arms of the vessel to displace the air. After this process the tubes were sealed off and the stoppers coated with de Khotinsky wax. The strength of the barium hydroxide electrolyte was determined by titration at the end of the measurements.

The cells were immersed in an oil-bath thermostat regulated to 25 ± 0.05°. The temperature was determined by a sensitive thermometer which had been checked against a Bureau of Standards thermometer. The electromotive force measurements were made with a Leeds and Northrup Type K potentiometer and Type R (2500-c) galvanometer. The standard cell was frequently checked against a Standard Weston cell with a Bureau of Standards certificate.

Results and Discussion

After five or six hours the cells were generally within several tenths of a millivolt of their equilibrium values, and values which proved to be the final ones were attained in one or two days. Table I, a, b and c presents the measured values of the potentials of cells of Type 3 where the lead monoxide was the hydrate, red and yellow forms, respectively. Cells 1 and 2 consisted of one pair of electrodes only. Where fewer than nine combinations for a given concentration are given, one or more of the electrodes proved insensitive or yielded constantly drifting values.

potash in a vacuum desiccator for one day. Their hydrate No. 10 ($PbO \cdot 0.470H_2O$), white without recognizable crystalline structure, was precipitated from potassium plumbite solutions by 33% acetic acid. After washing and filtering it was dried for three days over soda lime. There remained in the product 0.64% K_2O. Other preparations differed from No. 1 in later treatment and showed different proportions of water. One is left with the impression that the analysis, except for K_2O, etc., consisted in the determination of water content. Hydrate No. 5 ($PbO \cdot 1.218H_2O$) (same as No. 1 except that it was not dried after filtration) when subjected to isobaric dehydration at 10 mm. gave a flat in the water %–time curve corresponding to 0.5 mole of water per mole of lead monoxide. The loss of water below 0.5 mole they describe as "zeolithic" in character. They consider that both their dehydration experiments and x-ray analysis offer no indications of hydrates other than $2PbO \cdot H_2O$. Those of lower water content show tinges of color and in addition to the well-marked x-ray pattern of the semi-hydrate (No. 1), show weakly but nevertheless plainly the most important lead monoxide lines. If in the dehydration experiments the temperature rises to 100° the product is mainly the red form.

The theoretical percentages of lead in the hydrates $2PbO \cdot H_2O$, $2.5PbO \cdot H_2O$, $3PbO \cdot H_2O$ are 89.22, 89.93 and 90.39, respectively. The early papers reported the first and third of these. Glasstone[3,4] and Töpelmann[3] write the formula of the compound in the second form. Though the analysis of Randall and Spencer agrees exactly with that of Töpelmann, they write the formula in the form used by Pleissner and others, $3PbO \cdot H_2O$, and we shall also use this form in the present paper. It is unfortunate that the interesting experiments of Hüttig and Steiner were not carried out also with Pleissner's preparation and that their method of analysis is not stated. It seems highly probable that the composition of all the forms is the same.

Assuming the cell reactions indicated in the equations

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) + 1/3H_2O(\text{in } xM\ Ba(OH)_2) = PbO{\cdot}1/3H_2O(s) + Hg(l);\ \Delta F_{298.1} = -30{,}752 \text{ cal.} \quad (3a)$$

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) = PbO(\text{red}) + Hg(l);\ \Delta F^\circ_{298.1} = -30{,}985 \text{ cal.} \quad (3b)$$

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) = PbO(\text{yellow}) + Hg(l);\ \Delta F^\circ_{298.1} = -30{,}840 \text{ cal.} \quad (3c)$$

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Pb(in het. amalg.), PbO(red, yellow, or hydrate), $Ba(OH)_2(xM)$, HgO(red) + PbO(red, yellow or hydrate), Hg(l)

(a) Solid Phase, $PbO{\cdot}1/3H_2O$			(b) Solid Phase, PbO (red)			(c) Solid Phase, PbO (yellow)		
No.	Molality $Ba(OH)_2$	$E_{298.1}$	No.	Molality $Ba(OH)_2$	$E_{298.1}$	No.	Molality $Ba(OH)_2$	$E_{298.1}$
1	0.1054	0.66647	31	0.1540	0.67165	49	0.1650	0.66834
2	.1160	.66660	32	.1540	.67154	50	.1650	.66834
4	.1018	.66635	34	.1540	.67156	51	.1650	.66845
5	.1018	.66635	35	.1540	.67143	52	.1650	.66833
6	.1018	.66636	37	.1944	.67130	53	.1650	.66835
7	.1018	.66626	38	.1944	.67138	54	.1650	.66843
8	.1018	.66626	39	.1944	.67144	55	.2122	.66820
9	.1018	.66626	40	.1944	.67114	56	.2122	.66835
10	.1018	.66651	41	.1944	.67120	58	.2122	.66815
11	.1018	.66651	42	.1944	.67127	59	.2122	.66828
12	.1018	.66652	43	.1944	.67138	61	.2122	.66826
14	.05	.66632	44	.1944	.67147	62	.2122	.66839
15	.05	.66642	45	.1944	.67154			
16	.05	.66619				Average		.66832
Average		.66638	Average		.67141			

The free energy of formation of mercuric oxide was calculated by Lewis and Randall[10] from data of Brönsted, Ming Chow and Buehrer on the cell

$$H_2(g),\ \text{dil. NaOH or KOH},\ HgO,\ Hg \quad (4)$$

for which the standard electromotive force is 0.9265, 0.9264 and 0.9264 v., respectively. The free energy of formation of water necessary to obtain that of the mercuric oxide is partially dependent on the potential of this cell since Lewis and Randall's final value for water, −56,560 cal., is based on four sets of determinations, one involving the above cell and the less accurate value for the free energy of formation of mercuric oxide from direct dissociation measurements. This leads to

$$Hg(l) + 1/2O_2(g) = HgO;\ \Delta F^\circ_{298.1} = -13{,}808 \text{ cal. (prelim.)} \quad (5)$$

Ishikawa and Kimura[11] measured cells of Type 4 with 1.027 N sodium hydroxide as electrolyte at 0, 15, 25, 35 and 40°. They find after correction for the lower activity of water (0.33 to 0.42 mv.), $E^\circ = 0.92565 -$

[10] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 408, 477–485.

[11] F. Ishikawa and G. Kimura, *Sexagint, Y. Osaka, Chem. Inst. Dept. Science Kyoto Imp. Univ.*, 255 (1927).

$0.0002948\,(t-25) + 0.0000004991\,(t-25)^2$, where the mercuric oxide is the red form, a Kahlbaum product prepared from mercuric nitrate. Ishikawa and Kimura also used the yellow form (Merck product) and found after several days $E^\circ_{298.1} = 0.9263$ v. One of these cells was followed for fifteen days, by which time its potential had fallen to 0.9260 v., and was thus approaching the value gotten immediately with the red form. They point out that Brönsted and Miyamoto gave no description of the oxides used, that Ming Chow's was described as a "chemically pure commercial preparation," and that Fried[6] used a yellow precipitated oxide. The five cells at 25° gave values differing from the mean 0.92565 by 0.05 mv. Their equation leads to $\Delta S_{298.1}$ for the cell reaction equal to −13.60 E. U. A more significant check by the third law of thermodynamics can now be made. Using the following entropies: Hg, 18.3 (Rodebush and Rodebush), H_2O, 15.92 (Latimer and Greensfelder), H_2, 31.23 (Giauque), and HgO, S = 16.6 (Rodebush and Rodebush),[12] $\Delta S_{298.1}$ for the cell reaction is equal to −13.61 E. U. The check is closer than the uncertainty in the entropy values. ΔH of formation of mercuric oxide from the cell measurements and that of water, −68,313 cal., by Rossini[13] is −21,540, and is thus within the range of thermochemical values −20,700 by Nernst, −22,000, Thomsen, and −21,500 cal., Varet. We shall therefore accept the value of Ishikawa and Kimura, $\Delta F_{298.1} = -42{,}717$ cal., for cell 4 and combine it with the free energy of formation of water by Lewis and Randall (since their final value, the mean of all four values, is also the mean of those excluding that determined through mercuric oxide). Thus for Reaction 5, $\Delta F^\circ_{298.1} = -13{,}846$ cal.

Spencer and Randall[14] from a study of the data of Gerke, Hulett, Obata and others take

$$\mathrm{Pb} = \mathrm{Pb(in\ het.\ amalg.)};\quad E_{298.1} = 0.00586\ \mathrm{v.},\ \Delta F_{298.1} = -270\ \mathrm{cal.} \qquad (6)$$

Combination of Reactions 3a, 5(Ishikawa and Kimura), and 6 yields for the white hydrate of lead monoxide[15]

$$\mathrm{Pb(s)} + 1/2\mathrm{O_2(g)} + 1/3\mathrm{H_2O(l)} = \mathrm{PbO{\cdot}1/3H_2O(s)};\quad \Delta F^\circ_{298.1} = -44{,}868\ \mathrm{cal.} \qquad (7)$$

With less certainty, due to the problematical status of the formula of the hydrate, one may obtain the standard free energy of formation from the elements by combining Equation 7 with one-third the free energy of formation of water, *i. e.*, −18,853 cal. Thus

$$\mathrm{Pb(s)} + 2/3\mathrm{O_2(g)} + 1/3\mathrm{H_2(g)} = \mathrm{PbO{\cdot}1/3H_2O(s)};\quad \Delta F^\circ_{298.1} = -63{,}721\ \mathrm{cal.} \qquad (8)$$

[12] W. H. Rodebush and E. Rodebush, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, pp. 88, 90; W. M. Latimer and B. S. Greensfelder, *J. Am. Chem. Soc.*, **50**, 2202 (1928); W. F. Giauque, *ibid.*, **52**, 4816 (1930).

[13] F. D. Rossini, *Proc. Nat. Acad. Sci.*, **16**, 694 (1930).

[14] H. M. Spencer and M. Randall, unpublished data.

[15] The correction for the lower activity of water in the more concentrated barium hydroxide solutions has been estimated from freezing point measurements. Since its value, five calories, is less than the experimental error it has not been applied.

Combinations of Reactions 3b and 3c with 5 and 6 yield for the red and yellow forms of the monoxide

$$Pb(s) + 1/2O_2(g) = PbO(red); \quad \Delta F^\circ_{298.1} = -45{,}101 \text{ cal.} \qquad (9)$$
$$Pb(s) + 1/2O_2(g) = PbO(yellow; \quad \Delta F^\circ_{298.1} = -44{,}956 \text{ cal.} \qquad (10)$$

If $-13{,}808$ cal., the value for Reaction 5 by Lewis and Randall, is used, the values for Reactions 7, 9 and 10 are, respectively, $-44{,}830$, $-45{,}063$ and $-44{,}918$ cal.

The result of Reaction 9 is to be compared to $-45{,}050$ cal., from Smith and Woods' cell 1. Ishikawa and Shibata[16] have found for a similar cell, $\Delta F^\circ_{298.1} = -44{,}921$ cal. Unfortunately the nature of the lead monoxide used is not stated in the abstracts. Neither yields values of $\Delta S_{298.1}$ (-14.76, Smith and Woods and -18.46 E. U., Ishikawa and Shibata) in good agreement with the third law value, -17.06 E. U., based on the entropies at 25°, Pb, 15.55 (Ulich and Stackelberg),[17] PbO, 17.3 E. U. (Rodebush and Rodebush)[12] and those of hydrogen and water cited above. The modification involved in the specific heat measurements and the homogeneity of the samples are in doubt. Smith and Woods' cells do yield a value for the ΔH of formation of lead monoxide, $-52{,}403$ cal., using Rossini's[13] value for water, in good agreement with that of Werth and Eucken,[18] $-52{,}700 \pm 500$, whereas Ishikawa and Shibata's cells yield $-51{,}296$ cal.

The free energy contents of the white hydrate (aside from the water involved) and yellow anhydrous forms are greater than that of the red modification by 233 and 45 cal., respectively, whereas Randall and Spencer[3] found greater differences, 391 and 238 cal.

Summary

The free energies of formation at 25° of the various forms of lead monoxide, red and yellow, and the white hydrate, as they are based on that of mercuric oxide, have been determined from measurements of cells of the type

Pb(in het. amalg.) PbO(red, yellow or hydrate), dil. $Ba(OH)_2$, HgO(red) + PbO(red, yellow or hydrate), Hg(l)

The free energy of formation of the red modification is compared with that obtained through the hydrogen–mercuric oxide cells and the differences in free energy content of the various forms are compared with those derived from solubility measurements.

[16] F. Ishikawa and E. Shibata, *J. Chem. Soc. Japan*, **48**, 59 (1927), and *Science Repts., Tohôku Imp. Univ.*, [1] **18**, 109 (1929).

[17] H. Ulich and M. v. Stackelberg, Landolt–Börnstein "Tabellen," Erg. II, p. 1605, newly calculated with the results of Keesom and van den Ende.

[18] H. Werth and A. Eucken, Landolt–Börnstein, "Tabellen," Erg I, p. 837.